

INTERMOLECULAR INTERACTIONS FOR HYDROCARBONS ON WYODAK COAL

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INTRODUCTION

Low rank coals are abundant in the U.S.¹ Although their calorific values, mineral matter contents, and coking properties make them less desirable than higher rank coals in some industrial applications, low rank coals are used as feedstocks in coal liquefaction and are coprocessed with higher rank coals for other applications.^{2,3} The desire to use these coal resources more effectively would be aided by an understanding of the intermolecular and surface interactions at mineral-organic and organic-organic coal interfaces.

Studies of intermolecular forces in low rank coals have concentrated on the coals' ionic properties.⁴⁻¹⁰ Schafer quantified the ion-exchange groups in various low rank coals.⁴ From swelling studies Nishioka concluded that ionic forces play a role in determining the macromolecular structures of low rank coals.⁷ Ahsan et al. studied Wyodak coal's interactions with organic acids before and after the coal was demineralized by citric acid washing (CAW).⁸ They found that interactions with aromatic acids increased while those with aliphatic acids decreased as a result of demineralization. From pH studies of coal slurries Vorres found that a range of different ion-exchange sites exist in Wyodak coal.⁹ Martinez-Tarazona et al. showed that low rank coals possess ion-exchange sites in the form of both organic (carboxylate and phenolate) and inorganic (clay) components.¹⁰

In the present work, inverse gas chromatography (IGC) has been used to quantify the intermolecular forces of Wyodak subbituminous coal from the Argonne Premium Coal Sample Bank. It has been found that saturated and unsaturated hydrocarbons experience different intermolecular forces at the coal surface and that these molecules can be used to probe both specific and nonspecific forces in Wyodak coal.

EXPERIMENTAL

The procedure for IGC of coal surfaces has been described previously.¹¹ About 3g of coal of 40/60 mesh fraction is packed into a 1/8 inch O.D. stainless steel tube ~1.5m in length. GC columns are conditioned at the highest temperatures at which IGC experiments will be performed (150°C, 200°C, or 250°C). Experiments involve obtaining at least 5 peaks every 5-10 degrees over a column temperature range of at least 30 degrees.

Wyodak coal from the Argonne Premium Coal Sample Bank was used as the stationary phase.¹² The coal was extracted in tetrahydrofuran (THF) in a Soxhlet extractor for several days. Citric acid washing and HF-HCl demineralization procedures were those used previously.¹³ The alkylation procedure was that of Liotta et al.¹⁴ Adsorbate liquids and reagents were obtained from Aldrich at the highest purities available and used without additional purification. Adsorbate gases were obtained from Aldrich or from Matheson at purities of at least 99.99%.

RESULTS AND DISCUSSION

Figure 1 shows isosteric adsorption heats, q_{st} , for hydrocarbons interacting with Wyodak coal which has been heated to 150°C or 200°C.¹⁵ The data are plotted vs. molecular polarizability of the adsorbates, α' . The molecular polarizability is related to the electron distribution of the adsorbate molecule.¹⁶ For a given class of adsorbate molecules (eg., n-alkanes, chloroalkanes, 1-alkenes), α' increases linearly with increasing adsorbate size or increasing number of carbon atoms in the adsorbate molecule.¹⁶

The lower plot in Figure 1 shows data for n -alkanes on Wyodak coal. These types of adsorbates can interact with the coal by nonspecific van der Waals dispersion forces only. The adsorption heats for n -alkanes increase linearly with increasing adsorbate polarizability as expected for van der Waals interactions. The slope of the plot for n -alkanes in Figure 1 is a measure of the increase in dispersive van der Waals force with increasing adsorbate size.¹⁶ This information (the slope of the plot) is analogous to a dispersive surface tension, γ_s^d , which gives the strength of the van der Waals interaction normalized to the adsorbate area at a surface.¹⁷ The slope of the plot for n -alkanes in Figure 1 translates into a dispersive surface tension of 25 mJ/m². This is a fairly low dispersive surface tension, demonstrating that Wyodak coal presents a low energy surface to saturated hydrocarbons, similar to those found for hydrocarbon oils and bitumens.^{18,19}

The two upper plots in Figure 1 show data for 1-alkenes on Wyodak coal that has been heated at 150°C or at 200°C. Comparison of the upper plot, for the 150°C-heated coal, with the plot for n -alkanes demonstrates that alkenes have ~2-4 kcal/mol stronger interaction with the coal than n -alkanes. This difference is most likely the result of a specific interaction between alkenes and the coal, discussed below. The steeper slope of the plots for alkenes (upper plots) compared to the slope for alkanes (lower plot) reflects the stronger nonspecific van der Waals force experienced by alkenes at this surface.¹⁶ On oxidized carbon surfaces which contain polar functional groups, alkenes have more exothermic adsorption enthalpies than alkanes.²⁰ The stronger nonspecific interactions of alkenes on Wyodak coal likely involve interactions with polar groups on the coal.

As seen by comparing the two upper plots in Figure 1, heating the coal to 200°C causes a constant decrease in the adsorption heat exothermicities for 1-alkenes. The constant decrease in exothermicities of the alkenes' adsorption heats after heating the coal to 200°C suggests that a *specific* interaction between alkenes and the coal has been lost as a result of heating. Heating has caused the adsorption heats for all 1-alkenes to decrease by the same amount, -1.2 kcal/mol, while it has not changed the slope of the alkenes plot. A specific alkene-coal interaction, as opposed to a nonspecific van der Waals interaction, would be characterized by a constant change in adsorption heat for a particular adsorbate functional group-coal interaction. All of the 1-alkenes in Figure 1 possess a single double bond. Loss of a specific interaction between the double bond of alkenes with the coal surface would result in a constant decrease in the adsorption heat exothermicity. It is likely that a specific interaction is occurring between the double bond of the alkenes and ionic or polar groups on the coal surface. An interaction between the double bond of the hydrocarbon with a positive charge at a surface, a so-called "cation- π " interaction, could be responsible for the specific interactions between unsaturated hydrocarbons and Wyodak coal.¹⁶ Cation- π interactions occur in biological systems and at the surfaces of inorganic solids such as clays and silica.^{16,21} When the coal is demineralized by CAW or HF-HCl treatment, the same decrease in adsorption heat exothermicities (-1.2 kcal/mol; data not shown) occurs.¹⁸ This result provides evidence that removing ion-exchangeable cations from Wyodak coal results in the loss of a specific cation- π interaction which involves ion-exchange cations on the coal surface and the unsaturated bond of the hydrocarbon adsorbate.

Figure 2 shows data for n -alkanes and 1-alkenes interacting with the surface of Wyodak coal that has been heated at 250°C. It is seen that heating to 250°C results in the same plot of adsorption heat vs. polarizability for n -alkanes and 1-alkenes. Unlike the case for the 150°C-heated coal (Figure 1) where the different slopes of the plots show that alkanes and alkenes have different nonspecific interactions with the coal, the result in Figure 2 says that heating to 250°C gives the same nonspecific interaction for both types of hydrocarbons on Wyodak coal. Furthermore, a comparison of the data for alkenes on 200°C-heated Wyodak coal

(Figure 1) with data for alkenes on 250°C-heated Wyodak coal (Figure 2) shows that the adsorption heats for alkenes are similar on these two heated coals. These two heated coals have lost their specific interactions with the coal; therefore, this result says that the nonspecific component of the adsorption heat for alkenes is similar for 200°C-heated and 250°C-heated coals. On the other hand, the nonspecific component of the adsorption heat for alkanes has increased in exothermicity as a result of heating the coal to 250°C. The same result (same plot for alkanes and alkenes) is obtained by extracting or alkylating the coal (results not shown).¹³ The slope of the plot in Figure 2 corresponds to a dispersive surface tension of ~50 mJ/m². This value is similar to dispersive surface tensions found for flat carbonaceous surfaces.²² It was shown previously that extracting Illinois No. 6 coal or heating to 250°C gave a dispersive surface tension of ~50 mJ/m² for that coal as well.²³ These treatments cause changes in the concentration and/or polarizabilities of atoms at the coal surface.^{16,23} Changes in bulk coal properties have been reported to result from these treatments and it is possible that changes in the bulk are reflected as changes in the coal's dispersive surface tension.²⁴

CONCLUSION

In conclusion, IGC data show that three types of forces are experienced by hydrocarbons at the Wyodak coal surface: a nonspecific force experienced by n-alkanes, a nonspecific force experienced by 1-alkenes, and a specific force experienced by 1-alkenes. The nonspecific force felt by n-alkanes gives a dispersive surface tension of ~25 mJ/m² for this coal. The nonspecific force felt by 1-alkenes is stronger and likely involves interactions with polar groups at the coal surface. The specific interaction between alkenes and Wyodak coal is most likely due to an interaction of the unsaturated bond with ionic groups at the coal surface; i.e., a cation- π interaction. Heating the coal to 250°C increases the interactions with n-alkanes so that both types of hydrocarbons, alkanes and alkenes, have the same nonspecific interaction with the 250°C-heated coal. The nonspecific interaction with the 250°C-heated coal gives a dispersive surface tension of ~50 mJ/m².

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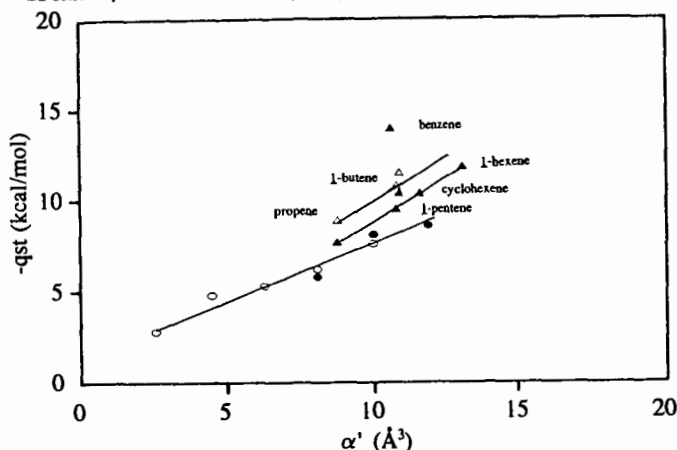


Figure 1. Isosteric adsorption heat (q_{st}) vs. adsorbate volume molecular polarizability (α') for *n*-alkanes, alkenes, and benzene on Wyodak coal heated in helium at 150°C and at 200°C.¹⁵ ○=*n*-alkanes (methane, ethane, propane, *n*-butane, and *n*-pentane) on 150°C-heated coal; ●=*n*-alkanes (*n*-butane, *n*-pentane, *n*-hexane) on 200°C-heated coal; △=*n*-alkenes on 150°C-heated coal; ▲=alkenes and benzene on 200°C-heated coal.

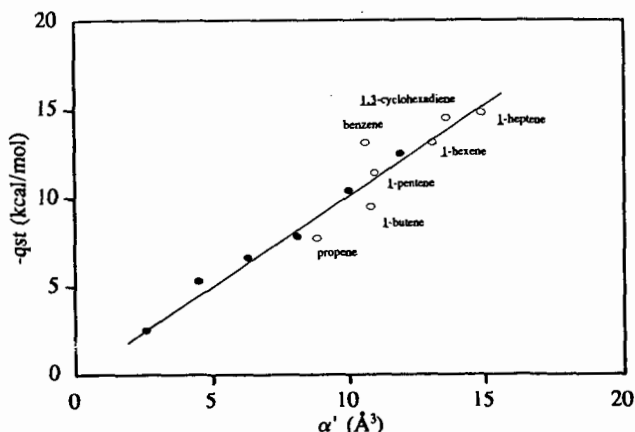


Figure 2. Isosteric adsorption heat (q_{st}) vs. molecular volume polarizability (α') for alkanes and unsaturated hydrocarbons on Wyodak coal heated to 250°C. ●=*n*-alkanes in order of increasing exothermicity: ethane, propane, *n*-butane, *n*-pentane, *n*-hexane, and *n*-heptane; ○=alkenes and aromatics on Wyodak coal heated at 250°C.